

L3 ANSWER 2 OF 2 WPIX (C) 2003 THOMSON DERWENT

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TI Production of hydrophobic disperse material - involves additional treatment with tetra-ethoxy- or-methoxy-silane or poly-methyl siloxane oligomer or poly-methyl silazane.

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The method of production of material, based on silica or metal oxide, includes activation of surface of starting material with carbonates of alkali metals, with mechanical mixing, and chemical modification with organometallic compound, at elevated temperature. To improve results, surface modification is conducted using elemental-organic compound of formula Cl_4-nSiR_n , where n is 1-3, and R is H, methyl-, ethyl-, Cl-methyl-, or phenyl-, and followed by additional treatment with compound selected from group including tetramethoxy-silane, tetraethoxy-silane, polymethyl (ethyl) siloxane oligomer and polymethyl silazane, in amount 0.5-1.0 wt.%.

USE - In oil and gas industry, as a method of chemical modification of highly disperse materials surface, to produce selective and protective properties. Produced materials can be used in oil and gas wells, to change oil- and water- permeability of strata. Application of chemically modified silica coatings onto elements of oil-gas complexes increases their resistance to aggressive media, corrosion, icing, biological growth etc.

ADVANTAGE - The method simplifies technology, intensifies process, reduces power consumption, and also increases hydrophobicity of product.

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METHOD OF PRODUCING HYDROPHOBIC DISPERSED SUBSTANCES
[SPOSOB POLUCHENIYA GIDROFOBNOGO DISPERSNOGO MATERIALA]

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Method of producing hydrophobic dispersed substances

Abstract

This invention pertains to the field of physical chemistry, specifically to the method of producing hydrophobic dispersed substances and it can be used in the oil and gas industry. The essence of the invention consists in the activation of silicon dioxide or metal oxides by the carbonates of alkaline metals by mechanical mixing and chemical modification of the surface at increased temperature using an organo-elemental compound with the general formula Cl_4-nSiR_n , where $n=1-3$; $R=H$, methyl-, ethyl-, Cl -metal-, phenyl-, with subsequent chemical treatment by a compound chosen from the group that consists of tetramethoxy silane or tetraethoxy silane, or an oligomer of polymethyl-ethyl)siloxane, or polymethylsilazane in the amount of 0.5-1.0 percent by weight. Chemical modification of the dispersed substance by the organo-elemental compound is carried out with their weight ratio (4-15):1 and temperature of 20-200 °C. The initial substance is subjected to preliminary drying to moisture content of not more than 1 percent by weight. Activation and modification of the surface are carried out with mechanical mixing of the components for 30-120 minutes, and the gas-like reaction products that form in the process are removed by blasting with an inert gas or by air through an alkali neutralizer. The method leads to a significant simplification of the process of chemical modification and production of an unexpected positive benefit reduction of energy expenditure by the factor 27-40 in comparison with the existing methods. Three claims, 1 table.

The invention pertains to the field of physical chemistry, /2*
specifically to the methods of chemical modification of the
surfaces of highly dispersed substances to impart to them selective
and protective action and it can be used in the oil and gas
industry. The use of these substances in boreholes changes the oil
and water permeability of the strata. The deposition of chemically
modified forms of silicon dioxide (CHMS) in the form of coatings on
components of oil and gas complexes improves the durability of the
latter with respect to chemically aggressive media, corrosion of
metals, freezing, overgrowing and liming. The coating of internal
surfaces of pipes with chemically modified silicon dioxides reduces
the hydraulic resistance of the moving fluids, which leads to a
reduction of the energy expenditures during transport. The
invention can also be used for imparting hydrophobic qualities to
solid powders, amorphous silicon dioxides for example, which are
used as components of water repellants for articles made of
ceramic, wood, paper, fabric, metals, brick, concrete and other
construction materials for the purpose of increasing their

*Number in the margin indicates pagination in the
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resistance to the elements and to improve their operational characteristics.

A method of chemical modification of silicon dioxides that are used for adsorption, heterogeneous catalysis, chromatography, as carriers for immobilization of enzymes, fillers of resins and rubbers, thickeners of plastic lubricant and so forth is known [1-2].

The process of chemical modification of amorphous silicas with the use of chlorine silanes is time consuming and includes the following stages

- Hydroxylation of the initial silicon dioxide (boiling in water, 24 hours);
- Removal of the physically adsorbed water from the surface of the carrier (1.3 Pa, 200 °C, 6-8 hours);
- Preliminary dehydration of organic solvents for the formation of easily mixed suspension with carrier and organic bases, which are used to bind the hydrogen chloride;
- Modification of the silicon dioxide in solutions for at least 8 hours at temperature of at least 95 °C;
- Extraction of the resulting product by dehydrated non-polar, and then polar solvents, including aqueous organic mixtures;

- Drying of the modified silicon dioxide.

A method of producing a hydrophobic dispersion, which includes surface treatment of the original substance (silica powder, silica filler, perlite, graphite, talc, asbestos, cement, mica or oxides of metals) by the hydroxide or carbonate of sodium, potassium or ammonia and subsequent chemical modification with the vapor of a silicon-organic compound on copper or brass lattices is closest to the proposed method (prototype) [3].

Shortcomings of the indicated method are:

a) Absence on the surface of chemically modified silicon dioxides of graft polysiloxane chains, which promote an increase of the water repellency of a substance and greater adhesion strength of the graft layer to the surface of the silicas;

b) The hydrogen chloride that forms as a result of the reaction is not removed from the reaction area, which leads to retardation of the chemical modification process, contamination of the environment and increased acidity of the resulting product.

The aim of this invention is simplification and speeding up of the process with reduction of energy expenditures, and also increased water repellency of the target product due to the

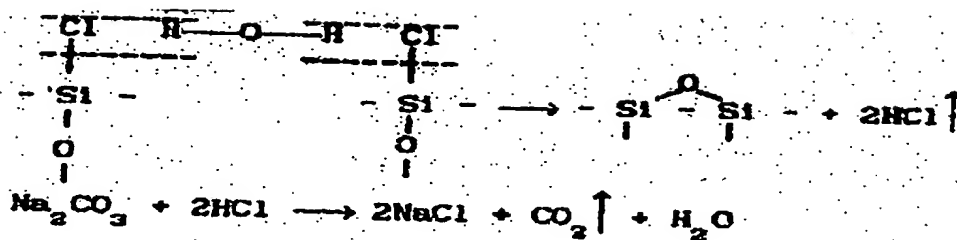
appearance on the surface of particles of graft polysiloxane chains.

The indicated goal is solved by a method that includes activation of the initial substance surface with mechanical mixing in the presence of solid alkaline metal carbonate and subsequent modification of the surface by an organoelemental compound at increased temperature, in which one uses according to the invention as the silicon organic compound a compound with the general formula $Cl_{4-n}SiR_n$, where $n=1-3$, $R=H$, methyl, ethyl, Cl-methyl, phenyl. The weight ratio of the mineral filler and organoelemental compound is (4-15):1. The initial substance is subjected to preliminary drying to a moisture content of at least 1 percent by weight. Activation and modification are conducted at 20-200 °C and with mechanical mixing for 30-120 minutes, and the gas-like reaction products formed in the process are removed by blasting with an inert gas or air.

The contents of the silicon organic compound used will depend on the structural characteristics of the modified silicas (size of particles, amount of surface area, diameter and volume of the pores).

The presence of a finely dispersed soda ash in this process /3 is a necessary condition for carrying out the dry method of chemical modification of silicas, because it fulfills two functions: 1) reaction catalyst and 2) pH regulator of the medium (neutralizes the HCl released). In addition to the gaseous CO₂ and H₂O that are released in the process of the dry CHMS method sodium chloride (NaCl) is formed, the presence of which does not lead to a noticeable reduction of water repellency of the new product. The use of such organic bases in place of soda ash, such as pyridine and triethylamine complicates the CHMS process, because in this case additional release of hydrochloric acid amine salts from the reaction products is necessary.

When using di- and trichlorosilanes as chemical modifiers of the surfaces of amorphous silicas the content of physically adsorbed water in the latter should not be more than 1% by weight. As results of elemental analysis and infrared spectroscopy of CHMS have shown, in this case there is additional condensation of the surface Si-Cl bonds with the sorption water



with the formation of polysiloxanes. Thus, the established minimal content of physically adsorbed water (0.5 .6 percent by weight) allows one to substantially expand the number of chemical surface modifiers used and, by applying the surface gathering method, to perform grafting in one stage.

In addition to silica, Cl-silane and sodium carbonate in the proposed ~~by~~ method of CHMS a fourth component is the synergistic addition, the presence of which in the reaction mixture in an amount of 0.5-1.0% by weight leads to an increase of the water repellency effect, and tetramethoxysilane, tetraethoxysilane, oligomers of polymethyl (ethyl) siloxanes, polymethylsilazanes and others can be used.

Example of specific fulfillment of the given method: 72% by weight of previously roasted Aerosila-380 at 150 °C with moisture content 0.5% by weight is loaded at room temperature into a reaction vessel and with stirring rod working gradually for 10-15

minutes one adds 7% by weight of finely ground soda ash. Mixing is continued another 15 minutes and slowly for 20 minutes one adds 20% by weight of trimethylchlorosilane. Then the reaction vessel temperature is raised to 55 °C and mixing is continued for 20 minutes. Monitoring of the reaction is carried out according to the released hydrogen chloride, which is passed through a neutralizer, filled with aqueous solution of alkali. In order to rid the reaction products of HCl the reactor is purged with an inert gas or air for 20 minutes. The departing gases at the end of the process should have a slightly acid reaction (pH 6-7). At the end of the reaction one adds 1% by weight of synergistic fluid (tetraethoxysilane) to the reactor and after 15 minutes of mixing the resulting product is unloaded.

The water repellency of the reaction product without considering the content of the NaCl that is formed was 99.6%. A study of the composition and structure of the chemically modified Aerosila was carried out by use of elemental analysis and infrared spectroscopy. Differences in the hydrogen content in the samples untreated and treated with sulfurous ester at its boiling temperature show that 95.2% of the trimethylchlorosilane used participates in chemical modification of the Aerosila surface

layer. The average concentration of the graft modifying groups on the SiO_2 surface is 3.97 micromoles/square meter or 2.39 group/square nanometer, which corresponds to a surface area value $A_m=0.49$ square nanometer for one trimethylsilyl group.

In the infrared spectrum of the modified silica, one observes a substantial reduction of the absorption strip of the free hydroxyl groups of 3750 cm^{-1} in comparison with the spectrum of the initial Aerosila and the appearance of the intensive absorption strip of the valence vibrations C-H_3 of trimethylsilyl groups at frequency of 2915 and 2975 cm^{-1} . The ratio $[(\text{CH}_3)_3\text{SiO}]/[\text{OH}]$ on the Aerosila surface is 0.55/0.45.

The trimethylsilyl groups, located alongside and over the hydroxyl groups remaining on the silica surface, form a surface layer with high level of water repellency as is evident from the derived results. The surface layer formed also has excellent thermal resistance. As the results of infrared spectroscopy show, heating of the Aerosila modified by this method in a vacuum up to $400\text{ }^\circ\text{C}$ does not remove the chemically graft trimethylsilyl groups from the surface.

temperature and reaction time 20 tests were conducted. Data on the conditions of chemical modification of the silicas by chlorosilanes and attained values of water repellency are given in the table.

It follows from the table that as a result of the silica modification conducted according to the developed method in all cases the formed modified products have a high level of water repellency, which reaches 99.0-99.6% (experiments 1-14). Small differences in the hydrogen content in the samples treated and not treated with ether show that in the majority of cases more than 95% of the used modifier participates in the formation of a single layer of graft molecules. Density of the layer grafted to the surface depends on the structure of the silica used and modifier content. Thus, in the case of using Aerosila-380 (tests 1-5) a high density of grafting is reached, which is more than 2 groups/square nanometer.

A different picture is observed during a change of conditions of silica modification. Thus, during an increase of the initial content of chlorosilane with respect to the silica (experiments 11-14) the differences in the hydrogen content increase in the product samples not treated and treated with ether. This indicates the

reduction of the percentage content of the modifier, which participates in formation of the graft layer of molecules of the alkyl(aryl)silyl groups. The concentration of modified groups on the silica surface in practice does not change (comparative experiments 2-14).

In experiment 15 of the table results are given for modification of the Aerosila in the absence of soda. As one can see from the table, under these conditions the modification-interaction reaction of the silyl groups of silica with chlorosilane occurs with great limits.

According to the proposed method of producing water repellent dispersed substance the modification of silica is conducted in the entire space of the reactor, but not on the surface of copper or brass gratings, as indicated in the prototype. This allows one to significantly speed up the process of chemical modification of silicas in productivity.

Information sources:

1. US Patent No. 4,209,432, Cl. C 08 L 83/04, published 1980.
2. British Patent No. 1,496,553, Cl. C 01 B 03/12, 1977.
3. Russian Federation patent No. 2,066,297, Cl. C 01 B 33/18, 1993.

CLAIMS

1. Method of producing water repellent dispersed substance on the basis of silicon dioxide or metal oxide, which includes activation of the initial substance surface by carbonates of alkaline metals during their mechanical mixing and chemical modification by an organoelemental compound at increased temperature, characterized by the fact that modification of the surface is carried out by organoelemental compound with the general formula $Cl_{4-n}SiR_n$, where $n=1-3$, $R=H$, methyl-, ethyl-, Cl-methyl-, phenyl-, with subsequent additional processing with a compound, selected from the group that consists of tetramethoxysilane, tetraethoxysilane, oligomer of polymethyl(ethyl)siloxane, polymethylsilazane in the amount of 0.5-1.0 percent by weight.

2. Method according to claim 1 characterized by the fact that chemical modification of the dispersed substance by an organoelemental compound is conducted with their weight ratio (4-15):1 and temperature of 20-200 °C.

3. Method according to Claim 1 characterized by the fact that the initial substance is previously subjected to drying to a moisture content of not more than 1% by weight.

4. Method according to Claim 1 characterized by the fact that the process of activation and chemical modification of the surface is carried out with mechanical mixing of components for 30-120 minutes, and the gaseous reaction products formed in this case are removed by purging by an inert gas or air through an alkali neutralizer.

Chemical modification of silicon dioxide by chlorosilanes

Experiment No.	prescription, weight by %			No, °C	reaction time, min.	water repellency, %	hydrogen content, % by weight		grafting density, N	
	silicon dioxide, metal oxide	modifier	Na ₂ CO ₃				untreated	treated with ether	micro-moles/m ²	groups/nanometers ²
1	AEROSILA-380, 72	TMKHS, 20	7.0	50-58	60	99.6	5.38	4.90	3.97	2.39
2	AEROSILA-380, 69	DMDKHS, 18	12.0	60-70	60	99.4	3.10	2.95	3.54	2.13
3	AEROSILA-380, 65	MTKHS, 20	14.0	55-65	60	99.2	1.51	1.42	3.41	2.05
4	AEROSILA-380, 87.5	DEDKHS, 19	12.5	120-130	75	99.3	5.90	5.62	3.47	2.09
5	AEROSILA-380, 69	MVDKHS, 18	12	85-94	50	99.4	4.67	4.44	3.60	2.17
6	AEROSILA-380, 65	FTKHS, 20	14.0	160-170	90	99.0	7.67	7.33	3.04	1.83
7	AEROSILA-175, 74	DMDKHS, 15	10.10	60-70	60	99.3	1.28	1.20	2.95	1.81
8	PERLITE, 73	DMDKHS, 15	9.0	60-70	75	99.5	1.01	0.95	2.57	1.53
10	SILICA FILLER, 73	DMDKHS, 15	10	60-70	30	99.4	0.80	0.72	2.54	1.54
11	SILICA DUST, 69	DMDKHS, 18	12	60-70	70	99.4	1.71	0.94	2.87	1.73

12	SILICA DUST, 72	DMDKHS, 12	5	60-70	70	99.0	1.28	0.93	2.85	1.71
13	SILICA DUST, 87.5	DMDKHS, 8.0	3.5	60-70	70	98.7	0.90	0.87	2.66	1.60
14	AEROSILA- 380, 61	DMDKHS, 24	14	60-70	60	99.5	4.87	2.99	3.60	2.17
15	AEROSILA- 380, 69	DMDKHS, 18	-	60-70	90	11.1	-	-	-	-
16	AEROSILA- 380, 69	DMDKHS, 18	12	60-70	120	99.4	3.08	3.00	3.60	2.15
17	AEROSILA- 300, 62	TMKHS, 20	7	50-58	55	99.2	5.12	4.85	3.90	2.35
18	AEROSILA- 300, 62	DMKHS, 20	7	30-36	45	99.3	3.09	2.99	3.54	2.12
19	TiO2, 88	TMKHS, 8	3	50-58	90	98.3	-	-	-	-
20	FeO3, ALPHA- FORM, 90.5	TMKHS, 7	2.5	50-58	90	97.9	2.78	2.60	2.84	1.70

Explanations to the table:

TMKHS trimethylchlorosilane, DMDKHS dimethyldichlorosilane, MTKHS methyltrichlorosilane,
 DEKHS diethyldichlorosilane, MVDKHS methylvinylidichlorosilane, FTKHS phenyltrichlorosilane,
 DMKHS dimethylchlorosilane.